© in 0 · C08F 4.44 · C08F 2/50 · C08G 65/12 · C08G 59/68 C08G 18/16 · C08G 18/22

G03F 7:00

C Application number 88307426.2 (2) Date of filing 11.06.68 (9) Date of publication of application

(E) Priority 28,08.87 US 90791

08.03.89 Bulletin 89/10

D Applicant MININESOTA MINING AND St. Paul, Minnesota 55133-3427(US) MANUFACTURING COMPANY 3M Center, P.O. Box 33427

Menufacturing Company 2501 Hudson Road (3) Inventor Brown-Wensley, Katherine A. Minnesota Mining and CH DE ES FR GB IT LI NL SE (E) Designated Contracting States

Manufacturing Company 2501 Hudson Road Manufacturing Company 2501 Hudson Road Intentior. Palazzotto, Michael C. Minnesota St. Paul Minnesota 55144-1000(U3) St. Paul Minnesota 55144-1000(US)

Inventor DeVoe, Robert J. Minnesota Mining

St. Paul Minnesota 56144,1000(US).

Popuesentative Battle, lain Cameron et al CO Lauss & Parry Isartorpiatz 5 D-6000 Munchen 2(DE)

E) Energy-induced curable compositions.

E. A pulymentable composition comprises a polyment, precitati autérior mais les proups dissating des as east one ethylenically unsaturated incinomer 2) at least this spirit remains that the thylenically unsaturated the distinct restriction of parameters of the complete company and the street of the

306 0

# BASHOY-HIGHCED CURVALE COMPOSITIONS

# Fleid of the Invention

nurumer an epoxy mondmer, or polyuretiens precursors, and as cuming agent a combination of an Jenometalic compound and an oxidizing agent and a method therefor: in another sepect, cured articles concursing the composition of the invention are decident. The compositions are useful, for example, as This invention rotates to an energy-polymentable composition compraing an ethylenically-unsaturated protective country, binders for magnetic mode or abreaves, achieves, and in graphic arts applications.

# **Lectpround Of The Invention**

consumental. These processes require a least catalyst or least nection promoter which can be Varous polyment costage and entities are produced in processes involving the use of organic coverts. There is an issuese effort by lew maters, researchers, and industr, is, promote high and 100% souch termulations to reduces or elements the ure of such solvents and the attendent costs and environment

as an the art. Curing of polymentable muture of polyreccyanates with polycia (referred to athere procursors) using thermally lettern catalysts is known in the art (see for example U. S. Themse cump of polyweitens precurers using nection promoters such as tin selfs and Pagest Nos. 4521.545, and 4.502.861). Caryanana a tao 100 11

Prozocumg of ureflues (methylocytess is use lanom (see T. A. Specthard, K.K.S. Hwang, S.B. Lin, S.Y. Tsay, M. Koenba, V.S. Ding, S.L. Cooper J. Appl. Polymer Science, 1985, 30, 647-698, C. Bluestein Polym -Past. Technical. Eng. 1881, 17 63-631, Priotocuming of polymerbane precursors using deconum selfs. ossoverages, sensitivity to expges, requirement of ultraviolet and/or high intensity light, the need for servey armos precursors, and organism compounds is also known (see U.S. Pasent Nos. 4,544,466. 4.549.945, and EP 20,000. Dervent abstract). At of these methods suffer from one or more of the following modified nears, tost or dilutes of unethers properties, for activity, poor solubility, and poor positie.

ne, such as famicians, can be used as a curing accelerator for appay materials (U.S. Patent No. sienes in the neichan between polyspointes and polyfunctional cumg additives, but they do not rasp-containing compositions not containing a curing additive. The sing materials is also become. Among such processes are those in 1,705.129) U.S. Pinget Non. 3,700,881, 3,714,006, 3,807,354 and 4,237,242 relate to the use of transitor The prox an discloses processes for the polymenization of epoxy materials. It is further known that a described in U.S. Passer Nr. 3,794,578 and U.S. Passet No. 4,080,274; hatonium salts as is decidend which the polymenization catalyst as a radiation-essessive chaim self of a Lewis and (e.g. diazonam selfs ( U.S. Passer No. 4,028,708; and the cours salts of Group VA elements, perfoundly the sulforum salts. as is checkned in U.S. Passet No. 4,085,081. These compositions are limited to ultraviolet radiation as decided in U.S. Papiet No. 4,058,400), or a dicadonyl chales compound of a Group IIA-VA elec polymenzaton. Furthermore, the decadorayl chalettes are morture samebre. HENZERON OF Sporte group-conta co-drad speeds to users-sewhod 

U.S. Pasers No. 4.216.286 sections the thermal cuming of calcology polymenizable compositions with On Sworper pur sters which

Energy purymentable compositions comprising lowic sales of enganometable complex calcons and and makingle and the curing thereof has been taught (see European Patent Nos. 108,851). 1964 Obt. 914 1803 Dervent abeleact; and 094,915, 1963, Dervent abeleact).

Lot the prodocuming of estylemically-unanticated monoment. (G. Brests, Pura G. Appl. Chem. 53,811,816 (1981), H.M. Wagner, M.D. Pubrick, J. Prodograph Science, 28, 220-226 (1981).
The use of contain photoseparation with online sales for entained of polymerization of estylemically. Neutral organometatic compounds have been used in combi

supercation copying, and other imaging systems (see .) Hoser in Light Benetive Systems: Chemistry and Accession of Nordawar Handa Photographic Processes, Wally, New York, 1986, pp. 166-160). Arybodonium

o-radiation in evaluation described for use as photomera are in addition-of

assurated monomers is also well known in the left technique has found applications in printing

able compositions. (See

Post of a

U.S. Paient Nos. 3,726,313, 3,741,756, 3,506,008, 4,226,228, 4,239,003 and 4,456,57, H. J. Timps and H. Baumenn, Wass Z. Tach. Nochech. Leane-Maresburg, 28, 430 (1994; H. Baumenn, G. Stenner, H.J. Timps and U. Lennind, J. Tack. Chem. 435 (3, 415 (1994; and H. Baumenn, U. Cerre and H.) Turps, Burn. J., 22 (4), 315 (4pxl.3, 1996).

# Purmeny of the Inventor

athylanically-unaskusasid monomer, or 2) at least one spony menomer, or 3) pelyunshane presure as curing agent a combination of a organometatic complexed and an online set. The complex upon a protective and decorative codings, whit, adheren, in restaints and seaton approxim mercathe composition comp dean provides an energy paly Driedy, the present ". maging applicat

nation with only made for the plants and electron beam-reduced comp of White is not laught in the prior art, but what is taught in this shreadon, is the use of org no procurers, and the the Advantages of compositions of the present invention when utilized in 108% resolve on of estrylerically-unestated monomers or polywests strylenically-unestrated monomers, appary most compounds in com

THE OF STREET, IN STREET, An industrial process ensembles is disclosed that will reduce. so varient waste white reducing energy of

sed organisms (seems or the prior proby reading in lower veccoety monemer schildone which are easier to cost than more vectors iton processing, perticularly utilizing electron beam and phini fore needby evaluate monomers can be used in place of functio capability for penetrating and polyme

ncreased flushility is despined contrast with specific properties iding the scope of curable monomers to enclude pelymocyc

omer solutions.

## in the application.

sers that polymenue by a free-radical mechanism recheson (witnesseles and works ecolerated particles (including electron beam), and framed (inferest and heat) means. er" meens a quantly sufficient to effect polyr unargy-induced curing" means curing by means of electromagn Campicony-effective and

proup is bonded to a metal auth ("Blace language Chamistry", F.A. Cotton, G. Williamson, Willey, New York connectable compound" means a chamical automate in which at least one carbon atom of an organneutration of the curation compos ton to a polymentard product at least to a degree to cause as increase in the incosety of the compession SA O AS

and" means a ligard that teach to time or mare means in the presence or absence of moto Topysebase pecuators' mass a minke of one or none menomers of the type actually of and polysocypeater, and one or man menomers of the type actually done and polysok. (
beging at less two exceptions-eactive hydrogen agains may be measured to date and polysok.) Mars 48000 12 to 21. of inc.; yands groups to incryandar-nacchie hydri 

polytocypania" means as alphaik or atomak, testyania hamig 2 or mos testyania groups polyof" magne an alighest or avenues companies companies 2 or more hydronyl gruspit, and conum acit" magne sella di caliane compounda such as daggorum, hatanum, and hypervali

# Detailed Decideure of the Inventor

procuron, and a bicomponent curry agent therefore, and in a second embedment a thermativ publi PROPERTY WONDERS OF DOSIGNATIONS PROPERTY seculty-unestrated monomer, or at least one ageny monomer. Or pathoon sons and a becomponent cump agent therefor, the cump agent in all cases comp The present mention provides, in a preferred emot menzable composition comprising at least one early 3 8 7 = 8

# The separation compound having the structure

HIXASENTS NOW OF 1 to 12 ligands contributing prefections that can be the same or different selected In substituted and unsubstituted acyclic and cyclic unsafurated compounds and groups and substituted unsunstituted carbocyclic aromatic and heterocyclic aromatic compounds, each capable of contributing The 24 presections to the valence shall of Mr.

represents none, or 1 to 24 ligands that can be the same or different contributing an even number of sugma-electrons selected from mone. Or, and thi-dentate ligands, each donating 2, 4, or 6 sigma-electrons

L'appresents none, it to 12 agands that can be the same or different, each contributing no more than one to the valence shall of lift: -

of coresents 1 to 4 of the same or different metal atoms selected from the elements of Periodic Groups IVB VB, VIB, VIB, and VIIIB (commonly referred to as transition metal:); some electron each to the velorice shell of each Mr.

with the proviso that said organometallic compounds contains at least one of a metal-me' 2 signs band and 1' and with the provide that L' L' L', and M are chosen so as to achieve a shible configuration; and

2) an onum sell oxidizing agent heang the structure:

.. ≯

3.794.576. 3.808.008. 4.628.708. 4.669.401, 4.688.685. 4.101.513, 4.216.288. 4.394.403, and 4.623.678, preferably selected from disponsism, loddonium, and sulfonium cations, more preferably A is selected from A is an ingaint cation selected from those described in U.S. Palent Nos. 3,706,296, 3,729,313, 3,741,799, cichen/todonum, inphonylaufonium and phanylbiophanyl diphenylaufonium; and

Pronotenzeneauforete and nistated isomers and the like, and those in which X has the formula DZ, wheren D is a metal from Groups (8 to Villa or a metal or metalfold from Groups (14 to VA of the Periodic Left." and SbCL." The curing agent can be present in the range of 0.1 to 20, preferably 0.1 to 10 weight X is an aniori, the counterion of the onlivin safes including those in which X is an organic authorsia, or percent of the total composition. The ratio of organometalitic compound to onlian salt is in the range of 10:1 Chart of Bernerta. Z is a halogen atom, and r is an integer having a value of 1 to 6. Preferably, the metalt prefereably are boron, standarian, andmony, bn. areanic, and phosphorous. Preferably, the halogen, Z. is GaCi., 146., 146., etc. Preferably, the amons are CV,80,, GF., Pf., SDF., SDF.ON chicane or fluores fluctrative of suitable arisons are OF1." PF1." Aef1." SDF1. FeCt." SnCh." SDF1. natogenesed mess or metafloid, such as are CN-803-1, CF-903-1, CAH-803-1, p-toluenesulfonese, ere copper. zmc. Hamum, vainadium, chromium, mengenese, iron, cobeit, or nickel and the metali to 1.10 by wargnt, preferably 5:1 to 1.5 by cought.

The present invention also provides a process for the polymentation of ethylenically-unsakurated hane precursors comprising the staps of: omers, or epoury mon

(a) providing at thest one ediplences by unexhanced monoment, or at least one appay compound, or polyurefrane precuration.

(b) adding to said compound a combination of a cassificatly effective amount of a curing agent comprising an organomatatic compound and an onlium sait (and all parmutations of the order of miching the storementioned components), thereby forming a polymerizable minuse, and

In a harder aspect, there is also provided a method for preparing costed articles containing the cured (c) aloung the number to polyments or adding energy to the minbut to affect polymentation.

composition of the invention comprising the staps of:

(a) pro-riding a substrate.

mentatible missure as described above onto at least one surface of said substrate by methods (mount in the art, each as har, leads, revense roll, trausled roll, or spin costings, or by dispong, spraying, brushing, and the like, with or without a coating schemi, and (b) committee an exercise por

(c) whiched overlight every suppose of eachers of present it present in the selecte to cause the properties of

in a suit further acced. Those are also provided shaped articles comparising the polymentable minture of casting, and extrusion. Applying energy to the menture causes polymerization and provides the Lund me invention. The anticles can be provided, for enampte, by techniques such as molding, injection molding

IT MAY be desirable to add solvent to solubilities components and aid in processing. Believed, preferable ganc solvent, in an amount up to 80 weight percent, but preferably in the range of 0 to 80 weight perce to composition can be used. was preferably in the range of 0 to 75 weight percent, of the polyment.

The valence metal-metal bending. We sum is governed by the "elgisses election nate" (see ), Chen. M. vanniscialer metal-metal bending. We sum in the same manual rate, "The effects register rate," In the There are restrictions on the total sum of electrons denoted by the **ligarit**s, L'. L<sup>2</sup>, L' of formule I and a total sum of 16, 17, 16, 18, or 20 elections in the valence shall are included utility the stage of the valence electrons possessed by the metal. For most organomatalite compensation not the compounds in which the sum of the elections donated by the figurals and the metal to aligh stimes called the "rate extent nat". The affection nam -matel bonding are described by formule I, in which carry stilled in the ert, however, know that there are exceptions to this rule and that organ heving a sum of 18, 17, 19, and 20 electrons are also brains. Therefore, or 48, 811 (1988); This rute is semestimes cathol Ste Train arbita-Tare gas rute". This rute states that the most states ongo

complexed motel cluster, MM, MMMA, or MMMAN has a tased pure of 30; 42, 44, 45, 45, 05, 07, 08, 08, 08, 06, THE PARTY OF THE WORLD inperture from the "eighten electron rule" can occur. It has then proposed (L. Armer, Charm. Sign. r compound 48 CVEs, and a seben-clear compound having sebenbeist, builtinft, and equip p y is seen to have 40, 52, or 44 CVEs, respectively. These stilling to "to ast, hearing, later billing to ness p orbits to so expert to came the places abother rath to these tra chater, chater valence electrons (CVE) are counted. A directors can validate for ligand bonding. Hence, rather than count electrons are 2 **1** 1 are are exceptions to this electron counting method and that ex ithiucher compound 48 CVEs, and a mineractuar compound he For compounds described in formule I in which interesand at at at 80 Over to a structure comp 5305 (1978)) that the department from the nown. Therefore, dl. th, or tetranicher ergan the to the metal-metal interactions dues

CVEs in the valunce shell, respectively, and are included within the apage of the in

Corecco

Coff (CO) Party

(COLAMISON (CO) MACAPIa

COO MATERION CO COCO MATERION

Corcola M-Carcola Corcola Mar Parcola Ca

(Callaccon Pres) 1400mp

741,1COls (1.10-phenanthroline)
Pe, (COls (1.10-phenanthroline)
Pe, (COls (2.2-biguinoline)

F. (CO) .

A.,1CO).

03,100),

RusiCO) - PPMs RusiCO) - o(Phy P-CHs CHs PPMs)

Fe, Ru(CO), 1

k.(CO).

Cofe, COLCOTA PR Cofe, COLCOTA PR Cofe, COLCOTA

Coccola Fe Fe(CO)(PFIts)(Co CoFe(COla (SiPla) 1Co. Fe(COb.)

Co(CO)side dap(CO)s (PPs) (Co Me, S.Copfille MeCopPates

Me is meety

Con a sea cycle P a prem

syl antectores as disclosed in U.S. Pases NO. ine trie-ecrytemists and them Becryster, the Dis-ecrysters and D o-, d-, or polyscrytates and methacryt THE TO RESIDENT SET Secondary des settol trimedlylacrylate, 1.4-cyclohes d and a spent, Ori l 4, XX4, 705. Managers of time or cases carromans can be used if desired. Overyl microsom, Chemyl Origina, thenyl principles, and ski Styl mediacytes, and very compa ers anch at mass of U.S. Paper No. 4.1 as of polyatelytees glycols of mot THE PERSON and/or obgomens puch as a DE D A Park 70 454212 -1 POT P 

of the polyweithers patenters that can be cured or polymerized in the and on in simulate grows inco the polymocyanate on hemocyclic poly

9

este hydrocesten redeel cor ate hudacates natical or hat at the So th cate days at most the no ton 6 to 15 cates from 2 to 100 carbon atoms, and ares to 10 hours from 4 to 100 carbon abone and same to 60 hates in which is as anyon 2 to 4, and 0 any that can be present in 0 archate hydrocarbon rastical oper eroment radical conta

Examples of poly nun-phosphero phone

DECEMBENO 1.208,788, U.S. PROPERTY OF Net Control ##. 2+ ##3 29## HEND-1-4 and -1-4-deacy ant No. 3.401,190), 2,4 and 2,6-hand ieocyanate, 1,3- and 1.4-phenytene di

encyaness describes in Brack Paper No. 674.480 Chaf No. 2504.48, 2577.65 are 2,602. STATE OF THE PARTY dry to U.S. Pages Ap. 34 are the 1484 life perpens To desire of the spirit THE PARTY AND LABOR. and or granted or the sectors Non 1,528,634 and 2,694,048, ougs of the type described, for example, in British Patent No. (BALER), in the rotomens disorperates according to U.S. Pasen No. 1/48,138, perjuscy U.S. Pagest No. 1567,755 and in Commer Pagest No. 1235 Alb. reacted ant Application No. 7,102,534, polytocypenses combining for example in U.S. Patent No. 3,091,673, so German Pa THE P. According to the present invention, it is also possible for ema # : # rigation reactions of the type described for event sectionnesed any polyleocyanates of the type deed in U.S. Petert No. 2,162,162 and in German Offenting rang eater groups of the type described, for e De. 3.124,606, 3.201,372 and 3.124,606 and in B esters according to U.S. Patent No. 3. 1,157,801 (U.S. Pet. No. 3,277,138, polytect) also with acastals according to Gas Nacytaneses con

8 2 . 1 possible to use desire itto posetble to use any mi

おなな 1007

The first preferably containing hydroxyl groups and generally containing from about 2 to 8, preferably struct 2 to 4 socyanish-reschie hydrogen atoms it is also possible to use minutes of different angle is not about 50 to 400. Examples of such compounds are ethylene given. 1.2- and 1.3- and 1.3- and 1.3- and 2.3-butylene given 1.1-forman doi.1.6-butane doi.1.6-butane.1.2.8-butane.1.3-butane.1.6-butane.1.1.8-butane

Office polycos suspice for the purposes of the present invention are the mutures of hydroxy additydes and vycory vestores. ("formion") or the polyhydric alcohole obtained thereform by reduction ("formion") which are formed in the presence of inself-compounds as a suspicious of emission of formidathyde hydrate in the presence of inself-compounds as a suspicious or polycome or accordance with a present invention (German Official polycytical and present and as the polycome or accordance with a present invention (German Official polycytical accident Mo. 2,638,759).

Many other compounds containing socyanate-nective hydrogen atoms and polysocyanates are useful in the present enventor, and are obvious to those stalled in the art of polyurethane science and technology.

Egony compounds that can be cured or polymerized in the dual systems by the curing agents of this inventor, using the latter in a catalytically effective amount, are those known to undergo catomic commission and include 1.2-1.3- and 1.4-cyclic auters (also designated as 1.2-1.3- and 1.4-epoxides). The 1.2-cyclic effects are preferred.

The cyclic enters which can be polymerated in accordance with this invention include those described in "Farg-Opening Polymeratedines", Vol. 2, by Frach and Reagan, Marcel Delater, Inc. (1989). Suitable 12-ryck: enters are the monominic and polymeric types of appointer. They can be applied, cyclodisphalor, accountry cannot see the applied; cyclodisphalor, and will typically have an approxy quantitative of from 1 to 6, preferably 1 to 3. Pertousiny useds are the applied; cyclodisphalor, and pyckely effect of broaders and as propylene, cyclodisphalor, which cyclodisphalor applied by cyclodisphalor and pyckely effect of broaders dought of cyclodisphalor and pyckely effect of broaders dought constructions and pyckely effect of broaders dought on epicies. A 3-4-pooxy-6-methylogisphalor and the cyclodisphalor dought of phenoitemediality of enter protect and epoch; shoones, e.g., demotifylator and having cyclodisphalor.

A wide versity of commercial again, regies are aveigbte and lead in "Handbook of Epony Reems" by the and heaville, leading the Company, New York (1987) and in "Epony Reem Technology" by P. F. Burns, John Melly & Song, New York (1988), Representative of the 1.3- and 1.4-cyclic others which can be commercial in accordance on the secondance of the commercial in accordance on the secondance of the commercial in accordance on the secondance of the commercial of the secondance of t

"DER-431" "Epi-Rec 521" and "DER-438", inspirated digitates less. "Kapanies", polygytod Hebburge (e.g. DER 7361) polysoyies spouds to g. Topocy. U-141, western modified apoints (e.g., THE STREET WENT OF CHARGE CLAMP Against. OF PROCESSES AMICH SAD and BROWN (SEE Life and and Brums, supras, Representative of the co-custives of herdeners which can be used and and CH135997, polytunctional Namble epoxides tog. "Fluxbaser 1817), and mindures thereof as well as premyl glyccyl other, 1.2-butese ande, diglycolyl ether of bispherol A (e.g., "Epon 628" in particular cyclic extent exich are neadily available include probylens oxide, custane, epichlorohydmi, vitedipate (e.g. EPL. propytame phosi to g. "ERL-4080" and "ERL-4062"), dipenient 90°: 1 s-bulariscosi digiricalyi ether 16-3. Acadas RD-2), polygycody ethir of phenolicimedethyde novolati versayorduran syrene cudo cyclohesenecude, verycyclohesene cude, glycidd, glycidyl methecryste House to g. "ERL-4288") apparatual polybranders to g. "Outon 2001"), secons oppiny to g. "Syt-Kem reycloneumecuntoriyasi selg. 1691-62217, 1.4-eposy-6-mathytycloneuyhnathyl. 1,4-eposy-6-ma ser, trates such as nadic methyl emhydnde cyclopentenesesesebouylic deshydnde, pyromi does tog. ER-4209, 3.4-sporjecyclohenytha ACCOMMENSATION OF THE ASSIST THE CONTRACTOR OF THE STATE 15 The professional carbonylic analytics, and medius thereof 1588, i sebutan eriory modylad eath poly and "DER 131"), umphopologisment OCTYMEN ON O

the store the imperiorestatic compounds useful or combination with online safe to provide the

## N DE SECTION

curing agents useful in the invention have the formule

L'L'L'M.

Ligands I. to I.3 are well known in the art of transition metal organization compared to I. are well known in the art of transition metal organization or polymetric compared frames a consisted group, i.e., an eithyletic. - C = C - group, assignment, C-C-C - group, assignment compared group, i.e., an eithyletic. - C = C - group, assignment C-C-C - group, assignment frame accessible preference registrates of the battle medical assignment of the compared is prepared) bearing the unstainant group is soluble in a resiston medical, such as an attorious organization or a teaton, e.g., methyl eithyl teatons an estima, e.g., annyl assistant, as an attorious e.g., interest or that the compound is chiefuld into very last practical or the action of the compound or distribution or an attorious or the action of the compared group is sufficiently close to a metal attain to the a proup or a proper compared, is metal, as experient below.

Mustake of ligard L' are the kneer and cyclic othyteks and activious compounds hemig less th sic; salamen, boron, enteriory, tefund cyclohopishians, cyclocollisiosans, and subsilisaed and unsubsilisaed carbocyclic and instruction busins, 2-busins, discoplans, buildiens, 1.2-dinathylacoplans, cyclobulans, parters, cyclopathins. actions, the cyclohomes onsatic figands heving up to 25 rings and up to 100 carbon atoms and up to 10 hours atoms schooled tropen, suitur, non-percuidic caygan, phosphorous, assenic, astenium, barca, antimony, tellunum, s cyclophene, 1,4-diphen/Bulene, earl-pyrrole, earl-thiophene, earl-faren, pyridhie, gammencolfine, e ans, cyclohesens, 12-cyclohesedens, cyclopentadens, 1,4-cyclohesedens, cyclohopisms, 1-octa (0) cation atoms, preferably heating less then 60 carbon atoms, and from zero to 10 hotero atoms s aboratera. Once sucable a structure, chrystene, pyrene, ett/-cycloheptebrenyi, triphenylmethene plane, chebenseite, 1 sum, and the, such as, for example, and-cyclopersadenys, became, meanylene, howerednys sillion, germentum, and the such as for example, otherwise acceptors, propriesss, dine, benzopyran, Briochroma, banzorazina, indole, acridina, carbazola, brphair ocians, 3,4-dimethyt-3-hausne, and 1-decens; etal-allyt, etal-pantarys, narbo compounds can be found by consulting any of many chemical handbodie. hom nategan, suiths, non-perceidic cargan, phosphorous, and tene, sibabanzene, 2.4.8-erphanytphosphabanzene. ene, phenotherane, set

As mentioned before, the ligand can be a unit of a polymer, for exemple, the phenyl group polystyrems, polytetyrems-co-busindens, polytetyrems-co-methyl methodylman, polytetyrems-co-busindens, polytetyrems-co-methyl methodylman, polytetyrems-co-methylman, polytetyrems-co-methylman, polytetyrems-co-methylman, polytetyrems-co-methodylman, polytetyrems-co-methodylm

Each ligand L' can be automited by groups that do not element with the completing of the light. The metal atom or which do not reduce the solutality of the ligand to the element that completing with the metal atom does not take place. Examples of automations, all of which presents that the light that cannot be a solutary group, all of which presents the test that the cannot be a solution atoms and to 10 heaten asserted from regions, all of which presents or proposed or a series, elements, and the cannot be a solution or a series, elements, and the cannot be a solution or a series and the cannot be a solution or a solution of the cannot be a solution or and the cannot be a solution and the cannot be a solution or and the cannot be a solution or and the cannot be a solution and the cannot b

indence and the like.

Each liquid L<sup>2</sup> in formula 1 is provided by monodestass and polydestass compounds preferably containing up to about 30 cation stores and up to 10 feeting atoms satisfact from introgen. Buffer non-perceidic cargon, procedure cargon, procedure cargon, procedure cargon, procedure cargon, setting to the first setting to the hydrogens, the polydestase compounds preferably forming mass atom, tolibusing loss of zero, one, or two hydrogens, the polydestase compounds preferably forming

adhybelency adhybellus; and brinsibylaticky; condensed imps auch as banko, cyclopents, nas

ANAPAS or groups are carbon monoride, carbon suifide, carbon selende, carbon tellunde, alcohols such butance and phenoi, narosonium (e.e. NO.), compounds of Group VA elements such as the metal M a 4-5-to 6-membered salurated or unsalurated mg. Examples of suitable monodentate Huchenystichne, Includychosphie, sonieries auch as phenysonerie, butysonerie; carbena groups ouch as ethogymethycatoone, difluomethosycatoone, allysidenee auch as methysidene, ethysidene, sustable Justic yandpropens, and hydrodropymacoyboress. The hydroxycarboxytic acids such as glycosic acid. Jactic conhoromethyl-12-detectors, animocontocytic acids such as alienne, glycine and o-animosenzoic acid; alcarbonytic demaiss as outsender, brundt diseanes such as 2,4-pentanedione, hydroxytistones such as 2demes such as selicylaidowne; helowines such as benzi owne; and phose in amonytanime, bimedyphosphine, hiphenylenime, biphenyphosphine, biphenyler JOSE/DESTARR COMPOUNDS of groups include 1.2-breidighenytphosphinojethene, 1.2-breidighenytereinojethene ACID SANCYNIC BOOK DONYNYGHIC GREATOR BUICK BE CARECTOL BIND 2.2 -CHTydroxybighlenyl; hydroxyamines such athen cynditions denience, increments such as eathy wanthers, phenyl wanthats; the definitions such as bis-SCAT, F1, OHT, CT, BT, IT, and HT and the organic groups such as, for example, acetoxy, and before, the ligard can be a unit of a polymer, for example the at, the phospharo group or poly(4-varytphenyldiphenylphosphae); the the groups are the marganic groups such as, for example, me, and 2-emmophenol; diffrocarbamates such as diethyldithocarbamate deshylenemenne. Cartoniyik and graup in polytanyin and; and the contral group in poly(4-virybhanytaonaria). eflytenechemine, propytenechemine, M. R. R. Distribution of the Company of the C otherotemes, properatem Marked a drop Sychiate and a damp 3

Sulebbe Agends (2) in formula I arclude any group heving in its shuckure an atom with 'n unshared electron. Suddible groups call contain any number of carbon atoms and hatero atoms but preferably contain ess then 30 carbon atoms and up to 10 hetero atoms selected from nárogen: "ulfur, oxygen, phosphorus, tetherum, articon, germanum, tm, and boron. Examples of such groups are hydrocarby groups auch as methyl, ethyl propyl, heryl, dodecyl, phenyl, solyl, etc.; unisakrased hydrocar-byl groups auch as venyl, etal-dulanyl, etal-cyclohanenyl; the hydrocarbyl denvatives of a Group hygemenyi, trohenyetenyi, and trmethytalyi, trohenytead, etc.; and organic provps such as formyt, aceigit, propionyt, acrytoyt, octadecoyt, benzoyt, tolunneuulionyt, cushyl, malonyt, o-A POR ST

to auticibe as L' 4 any group having in its structure hito, firse, or lour unshared elections, with the one emotion is shared per metal M. Examples of such groups are CHo, SiMer, SiPhy. 

can be any expinent from the Persons Groups MB, VB, VIB, WIB, and VIIIB, such as, for example, Ti. HE V. MD. To. C.: MD. W. MR. Tc. Pa. Fo. Pa. On Co. Rh. E. M. Per and Pt.

son of the polymonand or cured product. The amount of curing agent to be or polywelthers precursors into latest curing agores comprising an organometalic compound and an onlium safe can be carried out at norm temperature for the majority of energy curable compositions, although low Habers to g. - 10 C) of executed temperature (e.g., 30 to 200 C, preferably 50 to 150 C) can be used used in this invention shaud to sufficient to effect polymentation of the monomers or precuraors (i.e., a general, radiation-extraord polymenzation of ethylenically-unsalurated monomers, epoxy monomers, menzation or to accelerate the polymenzation, respectively; Temp. saure of ed all combyst out vary and be dependent on the persouler curable composition of accus 0 t to 29 upper partient, and professibly 0.1 to 10.0 upper percent, based on the weight of curable catalyticaty-effective amusely under the desired use conditions. Such impount generally will be in the range 

probled which can affect the cump of operates, polyweithers precurents, and whyl monomers. It is motorytes. Evidence for this feature of committee of provided for some organismissible compaints such as Cofe(CD), I and Mhu(CO)-; and emotions the abstraction of Cl from CCL subsequent to photolysis particidant, p. 138 j.m. other cases reactioacopic data provides such exidence (O. Hachelberg, A. Wojciclu J. LEG., R. G. Baverson, A. Wopcock J. Oogenomet. Chem. 1978;157-173). The city needs with the conduces again. By Bis process, the catalytic spaces White nor webring to be bound by simply, we propose that when specified organometallic compounds ere madellad is the presente of suitable orithang against such as onum tath, intermediate compounds are and chaves homolytically upon GEOTTOY AND WHIGHER. "Organometric Protochemetry" Academic Press. NY (1979) Chap 2 and 8. monomers is derived from the to the polymentation of the Ì ston metal or metal. some to superinded elegantical all tales to construct our ... The Part of Security PRODUCES OF this bond from

IP 0 208 161 A2

ol a carbonyl ligand, can occur. Such processes however, occur in such a manner as to such an entent the tree redical instators. It should be noted that compating or secondary photoprocesses, such as desocial the effective catalytic species and initiator are self produced so as to effect curing of the composition bond by one photon can ultimately load to the production of two organism

rethans (glyme), in some applications, it may be advantagedus to adsorb the curing agent onto an inert insatused monomer, the polyunethere precuracts, or the epony monomers, and as a processing an Representative solvents include accepine, methyl ethyl leatone, cyclopentarione, methyl celosolve acett metrylane chloride, intromethane, metryl formate, acatometrie, gamme-buryrolactone, and 1.2-dimes Solvents, preferably organic, can be used to asset in desolution of the cump agent in the ethyle support such as seleca, alumina, clays, etc., as desembed in U.S. Plasm No. 4,677,137.

a combination of an organometatic compound of Formula I and an onlian set of Formula II, any source o othylenically-unsalurated monomers, epoilly monomers, or polyurations precursors and as cuming agent a monomer, polyurethane precursors, or epoxy monomers, the thickness of the exposed material, type adapon including electron beem radation and radiation sources emitting active radiation in the ultra and wabble region of the spectrum (e.g., about 200 to 800 mm) can be used. Sustable sources of rad and concentrations of the organometatic compound and online sett, the perficular athylenically untail nctude mercury vapor decharge tampa, carbon arca, tungaten tempa, venon tempa, usern, sunt The required amount of exposure to effect polymenzation is dependent upon such factors as the For those compositions of the invention which are radiation-surething, i.e., the composisubstrate, intensity of the raciation source and amount of heat associated with the raciation

can be used to cure ethylenically-unsalurated or polyurethans precursors according to the teachings of the Thermal polymenization using direct heating or infrared electromagnetic radiation, as is known in the art

tuilly lower than those required for the cirect thermal curing, with an advantage in the range from 50 to quent heat-curing. These activised precursors may normally be cured at temperatures which are substanis within the scope of this invention to include two-stage polymerication (curing), by first activities C. This two-stage cumg also makes it possible to control the polymenization in a particularly ampli Curing the activities precursors so obtained, the irraduation temperature being below the temperature employed for the subs curing agent by irrachasing the cuitable compositions and subsequently thermally and advantageous manner.

agents, bodying agents, flating agents, colorants; mert fillers, binders, bloming agents, fungicides, bacsenocides, eurlactents, pleascusers, and other additioned as innown to those stuffed in the article to addited to Adjuvents such as solvents, proments, abrasive granules, stativicars, light stativicars, amboudants, flow the compositions of this invention. These can be added in an amount effective for their intended purpose

potting and encapsulated compounds, impregnating and coating compounds, and other applications which Compositure of this invention are useful for costings, foams, shaped arriches, adheemes, Med or reinforced composities, abreives, cauthing and seeling compounds, caeting and molding compounds are known to those stuffed in the art.

production of articles useful in the graphic arts such as printing plates and printed circuits. Methods of broducing printing plates and printed circuits from photopolymenting compositions are well known in the ari exposed may be weshed with a solvent to remove the unpolymenced purturns while leaving the phosopolymented, encoluble portions in place. Thus, compositions of this invention may be used in the Compositions of this invention may be applied, preferably as a liquid, to a substrate such as alumurm, copper, cadmum, znc. glass, paper, wood, or varous plessoc hims such as polyy sereptitusise), plessociad polykivnytichloride), polykjoropylene), polykjethylene), and the line, and 4 By polymenting part of the coaing, as by eraclation through a masti, those sections which have (see for example British Palent Specification No. 1,486,746).

Objects and advantages of this invention are further intustrated by the following examples, but the should not be construed to unduly limit this invention. In the examples, all parts are parts by earght unders particular materials and amounts thereof recited in these examples, as well as other concisions and detain indicated otherwise. All examples were propared in ambient atmosphere (presence of oxygen) and water unites indicated otherwise. In the examples

F - 3

Theuld - E

#### EXAMPLE

— iganimetalic compounds [CpFetCOlt]. Mhig(COlt), Rep(COlt) and [CpMetCOlt]s were obmitted to the compounds of the compounds were or and used without further purification. The other compounds were in any using standard organimetalitic symbolic techniques. The procedure used will be illustrated for the invariance of perfolicions.

The amon CpFe(CD): was produced by reducing 3.0g of [CpFe(CD)]s with 0.41g of soderim and "high" benzophanone in 200 mL of kesthy dealled kveshyritokuran under an amonophare of argoin. The mass allowed to proceed for about 24 hours by which time the starting metanish had all been minute amon as indicated by intered spectroscopy (R). To the solution of the amon was added, in a solid. The nection was stimed until the amol, was consumed as shown in the inaction vessel was operated to as and if the reducing mass indicated to starting as a solid. The nection was stimed under reduced pressure and column of solid beach in methylene chloride and passed down a short since get column. Crystats were blanced by removing the methylene chloride under reduced pressure and adding highere. The product was committed by R, nuclear metanism in fable I were prepared.

These compounds are used in subsequent examples.

#### TARE

| 5                                | Carameteron or compounds               | Compounds     |          |                   |
|----------------------------------|--|---------------|----------|-------------------|
| Clemen                           | Elementa: Analysis (Report/Calculated) | portCalculate | Q        |                   |
| Compound                         |  | Oy.           | <b>;</b> | Metung<br>Point C |
| Cofe(CO): SmPh,                  |  | 57 0/57.0     | 3.83.8   | 135-136           |
| Cofe(CO); Geffi,                 |  | 62.362.4      | 42.42    | 159-160           |
| CoferCOLPtens (CoferCOs Is SnPhs | COP & SAPPIN                           | 40.7/40.8     | 3.33.2   | 146-149           |
| (COLUMNSTAN)                     |  | 51.0/50.7     | 2.8.2.8  | 146-148           |
| (CON MAPPER) (CONMAND SAPI)      | L SarPhy                               | 30.939.8      | 1615     | 136-138           |
| (CO), Resorbh, Coltosofh,        | £                                      | 52.6/52.5     | 3.43.4   | 213-214           |
|                                  | ,                                      | į             |          |                   |

### EXMPLE 2

Several organization compounds were prepared according to Mariabie methods. CpW(CO),CH; was proceed according to the method of T.S. Pope, G. Wittinson, long, Muci. Chem., 1956, 3104-124. [CpW-CO),L was prepared according to the method of T.S. Pope, G. Wittinson, long, Muci. Chem., 1956, 3104-124. [CpW-CO),L was prepared according to the method of G. Censelli, E. Colone, P. Colon. 1978, 157, 238. [Chem., J. Organization of G. Censelli, E. Colone, P. Colon., W. E. Dougha, J. Organization Chem., 1977, 136, 373, 388. The method of J. P. Bober, A. Wolcich, J. Anner. Chem., 1977, 136, 373, 398. The method of J. P. Bober, A. Wolcich, J. Anner. Chem., 1977, 195, 373, 100 propers CoTe(CO), (CH;Ph), and that of R. B. High M. B. Bornelle J. Organization of H. B. Scholle, J. Dougham, 1984, 2, 15-37, to propers CoTe(CO), (CH;Ph), and that of R. B. High M. B. Bornelle J. Organization of J. B. Bornelle J. Organization of H. B. Michael J. Dougham, No. 4,800,464. These compounds are used in subsequent

#### XAMPLE 3

1.13 orwanizer flustrates the us 1 M an organization compound containing a transfer metal-transformation or the curing agent to photocotalyze the formation of polyurethere. A stock solution of a 1 methylenetralicy/coheuyheocyanae). (Desmodurity W, a Mobay Corp., Pittaburgh, PA) and 11 methylenetralicy/coheuyheocyanae). (Desmodurity W a Mobay Corp., Pittaburgh, PA) and 11 methylenetralicy/coheuyheocyanae. (Desmodurity and 0.02 g Phyl. PE = m.0.1 general-budyrotactore are acted 128 g of

# EP 0 306 161 A2

the stock solution. The sample was photocured to a solid using a Kodalthi Carousethi projector in 12 minutes.

Three samples were prepared as above, except the iron dimer and oddonum self were added as follows: sample (a), 0.01 g [CpFetCD)<sub>2</sub>b, 0.03 g Ph<sub>2</sub>l PF<sub>4</sub><sup>-</sup>, sample (b), 0.01 g [CpFetCD)<sub>2</sub>b, sample (c), 0.03 g Ph<sub>2</sub>l PF<sub>4</sub><sup>-</sup>; (a) was left in the dark while samples (b) and (c) were irradiated as above. Note of the three samples showed evidence of any cump, no obvious change in visiosely as evidence; safer 20

#### EXMPLE 4

This example illustrates the use of an organometalic compound containing a transition metal-carbon single bond in the curing agent to photocataly be formation of polyurathane. 0.52 ig Desmodur W (4 methylene bis (cyclotheryl socyanes)) and 0.72 ig Carbonez 400 (polyo) were combined and added to 0.01 ig CpPI(CH<sub>1</sub>)). (Cp. = etal-cyclopentadenyl) which had been disoched in ca. 0.15 not of a ministration CH<sub>1</sub>CI<sub>1</sub> and gamma-butyrolactione. The resulting ministrations was irradiated with a Nationalite 460 well medium pressure mercury arc lamp through Pyres1NL. Complete cure was achieved within 12 minutes irradiations.

#### EXAMPLE S

This example illustrates the photocuring of polyurethane precuracts to pulyurethanes in the presence and absence of O<sub>2</sub> using transition metal-transition metal bond containing organometaltic compounds and online salt as curing agent.

#### EXAMPLE 0

This example describes the photocumy of polyurethere precursors using transition metal-condiorganometalic chimpounds and iodonium and authorium salts. A stock solution was prepared from 7. Desmoûter W. 1.9 pers butanediol, and 0.5 perts transity/objectpans. Samples were prepared as in 2-ample 3 using 1.25 g of the stock solution. 0.01 g neutral metal-metal bonded compound and 0.015 g Phyl. Pfr.in 0.05 g germa-butyrdiscition. Irradiations were carried out on a 450 W Harrows medium pressuramercury are through Pyrex. Alternatively, these compositions can be cured thermathy.

#### TABLE

| 3            | Marage        | . S. F.   | 200<br>200<br>200<br>200<br>200<br>200<br>200<br>200<br>200<br>200 |
|--------------|---------------|-----------|--|
| Sufforment   | 3             | Pite! Pf. | 8.0<br>12-20<br>20-40<br>40-46<br>86-47                            |
| LOCORIUM ENG | Organometatic |           | Factors I  |

solving 10 mg caselyst and 20 mg ne for a scripte to become so viscous that it would not flow. "Partial cure" is indicated In off weed in 0.2 g CHCG. 2.0 g stock southon was added in th under a Hanous Quest URBy Lamp. The temperature of sample odur W and 32.8 g Carbon facth are establies in the curing agent for polyurethans in 10 min. The time to a viscocity such f was prepared by mining 23.1 g De **Ponent** cump agents tes were prepared by the The property of Stock solveton of on Ochemykoc CONTRACT BY

#### TABLE :

| Comp of Untillane Precurates | Cure Rates, min | Maccounty Current | 27 20 20 20 20 20 20 20 20 20 20 20 20 20 |
|------------------------------|-----------------|-------------------|---|
| 3                            | *               | *                 | Common control                            |

The data stow cutting occurs de dumpeo estates e apropri station and iomass

# EP 0 308 161 A2

## EXMENES

td by desolving 10 mg cas polymer was tested by placing a few drops of the sample in about 2 ns mathena. Formation of preci horophosphese (if used) in 0.2 g Cht.Cs. 2.0 g cycluh indicated that polymer had formed. Further polymenzation resulted in a vacocity incre lidded in the dark, and semples were then irradiated under a He the use of the curing agent con Results are indicated in Table IV. This example describes

#### TABLE IV

| Precipitate Vecceny formed, min. encreased min. | 10 Cue<br>35<br>3<br>3<br>3<br>3<br>3<br>3<br>3<br>3<br>3<br>3<br>3<br>3<br>3<br>3<br>3<br>3<br>3<br>3        |
|---|---|
| Cumg Agent Precipita                            | CpPtMss moonum 35 CpPtMss wodonum 35 CpW(CO)sMs wodonum 3 (PMss PN)sPMssuceres) + Pf 2 [CpFe(CO)s + rodonum 2 |

a included for purposes of compension

## EXAMPLE

and warm carried and under mutahand light, 0.3g o 1 01 0 10 a to to s (388 Company, recrysta ses (3 mil) polyvery on Carbide Company) w T to cure the con had to program the counting solution. The solutions were county onto 78 more that is the time needed to cure the costing so that when it is to Mactona, 20g cyclohemene omide (Alda nds and orman seat to ph : compound endor 0.20g dipheny in air, to a 275 mat Q.E. sactores at a di and out in the tollor chicride subbed polyeener (3M Com

## EP 0 308 161 A2

TABLEV

| Photomhetic     | on of Epony Cure      |           |
|-----------------|-----------------------|-----------|
| Compound        | 200                   | Time      |
|                 | No Onum<br>Saft Added | Omum Satt |
| [Cofe(COle)     | 01 <                  | -         |
| Cofo(CO), Seffs | 07.                   | <b>S</b>  |
| CoFe(CO); GePhy | V 0                   | wn        |
| Corector harm   | > 10                  | ,<br>     |
| May (OO)        | 0.4                   | -         |
| (CO): MargarPha | 2                     | •         |
| (CO) Mark Safte | -                     | •         |
| Re-100he        | •                     | 1.5       |
| Cotto(CO) SmPh. |                       | *         |

a time in manufact to cure

## EXAMPLE 10

ydodumone and stored cold und ready for use. Cyclohexene oxide was used as counsel from Albech. The organometatic compounds were obtained from commercial sources son. The organometatic compound, with and without the onlyin sa ess phospyzad in presence of an epoxy or acrytate. The specific system used is as follows: med Acceptosphere was recrystalized from acetone-tacpropanol. All experiments w To further demonstrate the activity of the cump agent, a series of e another apolity and/or acrytate compor

call along with 2 g of the depined monomer. For the acrytere tests, the solutions were purged with My for 60 cult along with 2 g of the deprived monomers from whe way years were performed without purging, water before and consequently during the photodysta. The epoint fluorescent bulb, in Table VI below, the curr I was mas placed 0.02 g of the organometallic compound withwithout 0.04 g of the indonlum Alternatively, the compositions can be cured their York as 100% solids, except as noted.

### TABLE Y

TO SECOND

|                     | Anima          | *****   |
|---------------------|----------------|---|
|                     | Ì              | *****   |
| Protestated Outs Te | Compyet System | Co-COD-<br>Co-COD-<br>Co-COD-<br>Co-COD-<br>Co-COD-<br>Co-COD-<br>Co-COD-<br>Co-COD-<br>Co-COD-<br>Co-COD-<br>Co-COD- |

C Peached in the dark o S TO SOLD

EXAMPLE 11

second sheet of pol 0.05g of the d

#### TABLE VI

| y Unseavesed Monomers | Cure Time*                | No Onum Onum Sat<br>Set Added Added | >600         | <u>.</u>        | :               |                  |           | 900             |                | -       | × 000 ×       | _                 |
|-----------------------|---------------------------|-------------------------------------|--------------|-----------------|-----------------|------------------|-----------|-----------------|----------------|---------|---------------|-------------------|
| Curing of Ethyrences  | Organometatic<br>Compound | * =                                 | (CoffeeObb b | Cofe(CO)s Smfn, | Cofe(COB-Geffi) | Cofe(COb ) Softs | Mr.(CO).e | (CO), ManSanthy | (CO) May Saptu | Pr(CO). | [Coltaccols b | Contract Contract |

a time in seconds to cure.

b sahrated solution, <0.01g desolved.

## EXAMPLE 12

Further examples of the curing of ethylenically unsakusted monomer (25 g of pentaerythritol lect activities in 225g acceptatible or appery monomer (cyclohausna cards) are provided here. A curable ned at 0.01g at the argenometatic compound or 0.02g of alphenyliadonium hexso same amounts of both compounds added to either chromer. The light sources net G.E. Discission builds and for the wardle, a Kodali son of polymenzation was detected by ously during inteclation while the cationic samples were left open to the air without purging. Sample sass tion of the polymer from a 2% ammonamethand solution. Free tablest systems were purged with Ny for 2 minutes before and contrus Ass 2 to 3 mL in a 13 a 100 mm pyrew test tube. The results of these tests are shown in Table VIII. and for the apony the precipital used were for UV exposure, about 360 rest, two 15 source german for the acrys ATLANCOPHOROPHIES OF EN composition commit

## TABLE VIII

A U de 101 A

| Acryses Compositors     |       |                |
|-------------------------|-------|----------------|
| Cump Agent              | Epomy | Acrysta        |
| [CoFe(CO) <sub>b</sub>  | 2,808 | <b>66</b> <    |
| (Cofe(CO)) is codornum  | » »   | ,80E <         |
| Mr <sub>2</sub> (CO). o | × 180 | <b>⊕</b> 01 >  |
| Mate (CO): e-rodomern*  | >100  | <b>-04&gt;</b> |

a Cure times given in seconds

b Unfinered projector as light sou c The diphenytodomum sell shor

taef under these same condition

e Blacktine used as the light source, ca 360 nm toud eas again poon regal way gay D

## EXMINE 13

projector, with a 300 nm cutoff lifter, and the time required ticure the sample recovided in Ta the photocatalyst systems. Semples were bubbled with My, and prechated wang a Mox sons can be cured thermaty. ACCE TO complex and 0.015 g Phyl PF. - Up to 0.05 g budy Semples were prepared as 1.0 g med Examples of the photocumg of ethyla metal bond containing organo

#### TABLE IX

| Compound Condense Cure Time and Page 1 for |
|--|
| CostCO)s Dark Cures during department  |

## EXAMPLE :

ses the curing of ethylenically-uneature onegounds. Each sample was proper

in the emove oxygen. Samples were then intachated in front of a foodal Carouasi Projector containing a this tim cutoff little, it no culting occurred in 16 mm, the semple was then aradiated for 15 mm under a street to remove unideters) was added in the dark and integen was buddled through the sample for 2 Service Quartz Unitry lamp In Table X. "cure time" resert to the time required for a sample to solidity . Leave with the short of the second of the

| Monomer   |  |
|---|--|
| Curry Agent   | Cure time, min   |
| CpPMAs<br>CpPMAs + icdonum<br>CpMCOsMa<br>CpMCOsMa + icdonum<br>CpMCOsMa + icdonum<br>CpPmCOsMa + icdonum | 15 (Nemonta)<br>8 (Kodek)<br>no cure<br>15<br>05 (dert cure) |

dichenyhodonum heisikuorophosphese (if used) in 0.25 g genme-bulyrolactone, to which was added 2.0 g amby), modified with a 300 nm filter. With a unefilme precursor stock solution (prepared as in Example 4), nonomer in a wall tradiation was then performed with a Kodati Carousel Projector (9 inches in the presence or absence of onlum self, partial curing to produce a clear solution, occurred in 2 hou reachation time. Upon planding in room light for 24 hours, an increase in viscosity occurred. example describes the use of (CpWICO)), to cure

When cyclohemeneade mas used, and the curing agent consisted of [CpW(CD)]; onlyin an sal vigorous, exoflermic curing occurred within 3 min of irradiation. When methyl acryste wis used as monomer, no curing occurred in the absence of onliam salt. With

20.g of polywethere precured or monomer was added in reduced light, the visit was capped, and the sample vradused on front of a Kodett Caroused projector filled with a 380 nm cutoff filler at a distance of nin Inches, and at room temperature (about 25 °C). Particular details and any experimental variations an gamma-curyrolactone were gordly agrated until dissolution of the organometalic compound has complete monomers for the case where the organometallic compound contains a single bond between a transi and, the following somples were prepared. In a visi, 0.01 g of organomes To demonstrate the usity of the curing agent for curing of poly metal and a Group IV stem compound, 0.02 g of dipher

# W . . . . . . . . . .

Precursors, Spories and vinyl Mondmers with Transition Hetal Cure Times: Photoinitiated Curing of Polyerethens

| Vient <sup>3</sup> | 2            | 1.0 edg               | RO 03             | a 23 mis                 | ٠               | 3                              |                  | 6 3d 8                    | 80 CME.          | ala no cure               | STRO CE          | BO CUE                    | no cure          | eano ou a                      |
|--------------------|--------------|-----------------------|-------------------|--------------------------|-----------------|--------------------------------|------------------|---------------------------|------------------|---------------------------|------------------|---------------------------|------------------|--------------------------------|
| A TROOTS           | J .(M)       | DOS OF (AA)           | 3 6               | (V) 12 min               |                 | (V) 5 min                      | 3 4(2)           | (V)h S min                | 3 q(A)           | 2.73                      | 3 q(s)           | (V)b 2 min                | (S)h £           | 33 min (W) <sup>h</sup> no cur |
| Urethane           | 120 min (w)  | (AA) ulu 09 pmp       |                   | •                        | 120 min (V)     |                                |                  |                           |                  | odonium 36 min (V)        | .*·              |                           | 45 min (S)h      |                                |
| Curing agent       | (cpre(co)2)2 | (Cpre(CO)2)2/10dontum | cpre(co),(cm,rch) | Cpre(CO),(CH2Ph)/lodoniu | Cpre(co),(corh) | CpFe(CD) 2 (COPh) / lodo linum | CpFe(CO)2(SiPh1) | CpFe(CO)2(SIPha)/lodonium | Cpfe(CO)2(GePh1) | CpFe(CO),(GEPh,)/iodonium | Cpre(CO),(Sarh,) | Cpre(CO)2(SnPh3)/iodonium | Cpre(CO)2(PbPh3) | Cpre(CO), (PbPh,)/lodonium     |

- Carbowax 400. Cure times are followed by an indication in parentheses of extent of cure, where V . viscous, VV consisting of 23.1 g of Desmodur TH W and 32.6 g of Polyurethane precursors are from a stock solution - v ry viacous, 8 - solid.
- Monomer is cyclobenene oxide, purified by distillation. Cure time is defined as the time necessary to observe f rmation of precipitate when one drop of sample is placed in 2 mt of methanol.
- through the polution for 2 min, with care being taken to prevent any light from reaching the sample during Monomer is mothyl act, late, purified prior to use by distillation under reduced pressure. After monomer solution viscosity of a sudden exotherm indicating rapid polymerisation (also accompanied by a sudden deoxygenated by bubbling a stream of nitrogen gas xygenation. Cure is defined by an increase in addition but before irradiation, samples were increase in viscosity).
  - Included for purposes of comparison to data in other rables.
- 60 min irradiation with Carousel Projector, followed by 60 minutes of trradiation in room (fluorescent) light.
  - This particular combination was not tested.
- 30 minutes irradiation with Kedak projector, following Utility Lamp (6 inches from bulb), followed by sample by 30 minutes irradiation under a Manovia Quartz storage/irradiation in room (fluorescent) light.
  - Irradiation with Hamowia Quartz Utility Lamp (15 cm from bulb) in place of the Kodak Projector.

# EXAMPLE 17 toungers

morromers using the curing again (Coffe(CO)) (After Pf. This example dustrates the dust custy of poly

Samples 125 g in size, were prepared from stock exhibites of 200 pars Desmodurita W (4.4stycal 6400 - 400, 6.0 parts methy acytetic hearty distilled), and 0.05 parts [CoFe(CO)s]s. To half of this stack schilles was added 0.000 parts Phel Hally Harachatcycloheryteocyanaeth. 242 parte polyadyte

## EP 0 308 161 A2

PF(\*) Mose raises for indonum satisfon dimer = 2.1, NCOOH = 10, weight % you dimer = 0.4%, indonum sat = 1.2%. Semples were insidered simultaneously veting 306 nm Blash? y bubs (15 weills) for 10 mm, then analyzed by 400 MAts. Hi nuclear magnetic resonance spectroscopy. Conver Table XI

#### TABLE XII

|  | ion to Perymer | Under | £     | £        | £                       | = | é           | ğ                       |
|--|----------------|-------|-------|----------|-------------------------|---|-------------|-------------------------|
| Precurators A  | Commercia      | Acry  | ŧ.    | £        | É                       | É | £           | 1                       |
| Dust Curing of Polyurethers !<br>Ethylenically-Unestited | Conditions     |       | Clerk | madleton | stadleton, decrygenesed | 1 | erradiation | mediation, decorporated |
| 8  | Se Se          |       | _     | _        |                         |   | - None      |                         |

# EXAMPLE 18 (company

ered. To a 10g sample of this minime was added 0.0kg of (Cyffo(CO<sub>IL)</sub>) or libe;(CO)<sub>1+</sub> o - 1000 = 000 et 1 in lines will not stow that both appromers have reacted at the same time. It is pot counts of both compounds, to a small visit was placed 2 at of th Maria the state of the state of the Maria est was carried out in the following manner: A VV, www, A usty during madeson. The la co spectroscopy to diffe aten. The emount of poly

#### TABLE OF

| M 100 M                 | Acryana      | = 8 % g >   |
|-------------------------|--------------|-------------|
|                         | (com)        | 6 พ ซ ซี ห  |
| Percent Connection to P | Caring Agent | TOP-ACCOUNT |

a theft's man by on a 400 little and

to None detected in the MASS.

As can to seem team the heaft nearly, and system official

# EXAMPLE 19 (comparative)

The promoted periodicities the simulationic curing of othylemically unsaturated and oppiny monomers 1 is ssimilable system. The curable unique-tion consists of methyl acrytes, cyclohexene oxide and THE STATE OF THE PROPERTY OF ACTIVES CUTE ATTEMPTED, then this system will produce a soluble perimer Only if both epoxy and acrytere cure are initiated wiff a crosslinked insoluble polymer be

Sample proparations main canned out under subdued lights. The polymentable murture consisted of 0.2 g jamma-outviacrona. 1 0 g glycodyl acrytata. 5 0 g mathyt acrytata and 5.0 g cycloharana oxide. Depending on me test added to this were 0.05 g of the desired organismetallic compound and/or 0.1 g dichenyhodonum heuskionophospheis. A 3 g ponton of this composition was placed in a glass wal and Harto seceration distance 4 cm). The semple was purged with neogen for one minute preceeding and As monomers were distilled before use; methyl acrylete and glycidyl acrylete from hydroquinone HELMHOO DAMMEN IND 15 WELL GESTEIN PLONECON DUBS USING ON UREWORK Products lamp holder controvously during pholohysis. The imadesion time required to produce a polymer insoluble in chloroform \* as recorded and is noted in Table XIV.

Attornatively, these compositions can be cured thermally.

#### TABLE XIV

| Smutteneous Protomeneon of Free Redical ( Epony Cure in a Cruusimtable System | Laterate System        | Padical and<br>ystem |
|---|------------------------|----------------------|
| Compound  | 3                      | Time                 |
| •   | No Onlum<br>Salt Added | Onsum Salt<br>Added  |
| [Cofe(CO); ]  | V 15                   | -                    |
| Cofe(CO): SnPh.   | × 15                   | 9 :                  |
| Cofe(CO); GePh.   | ×15 ·                  | . 51                 |
| Cofe(CO) b SmPhy  | . × 15                 | 2                    |
| May(CO):  | > 15                   | . 5                  |
| (CU), MASONTO,  | > 15                   | 9                    |
| (CO), Man J. Starth,  | 01 4                   | •                    |
| Per(CO).e   | >10                    | <br>S                |
| Cotto COP P   | > 15                   | 1.5                  |
| Control of the Control  | >15                    | 9                    |

Duhamylodomum hexafluorophosphate alone under these conditions did a time in menutes to produce insoluble crossimised system. not produce a crossinshed system after 15 mnutes. b Oxey 0.01g of the compound was used. Various modifications (and attentions of this invention will become apparent to those stulled in the art without departing born the acape and spirit of this invention, and it should be understood that this invention is not to be unduly timed to it. . Australiae embodiments set forth herein.

#### 2

1. A polymericable composation comprising one class of polyment precursors selected from the group specially-unsalurated monomer. 2) at least one apoxy monomer, and 3) priving the precursors, and a cump agent compraint in organomatatic compound and an onlimit salt, en and teach to it to gnasismi. MANUSCONDINA & SOMEON

2. The composition acroading to claim 1 effects is photopoly

# TO SEE SEE

- 3. The composition according to claim 1 wherein said class of polyment precurators in all least one etrylenically-unsalurated monomer or polyurethere precursors and said composition is thermally polymenzable
  - 4. The composition according to claims 1 to 3 wherein said organometatic compound has the formats.

#### M; I; I;

- L'ingresents none, or 1 to 12 ligands confibuling pi-elections des can be die same or different ligan selected from substituted and unautostituted scyclic and cyclic unestimates compounds and groups at substituted and unsubstituted carbocyclic aromatic and haterocyclic aromatic compounds, each cap
  - signa-electrons selected from mono. do, and thi-dentals ligards, each donating 2, 4, or 8 signa-electron Li represents none, or 1 to 24 ligands that can be the same or different contributing an even number contributing 2 to 24 presections to the valence shell of Mt.
    - Li represents none, or 1 to 12 ligands that can be the same or different, each contributing no to the valence shell of Mr.
      - one sigma-electron each to the valence shell of each lit.
- Ligands I'. I?, and I' can be bridging or non-bridging ligands: M represents 1 to 4 of the same or different metal atom selected from the elec
- mess-mess signs band and L2, and with the proves that L1, L2, L3, and M are chosen as as to achieve a VB, VB, VIB, and VIB, with the province that said organismatelic compound contains at least one of a and of Perodic Groups MG
  - 5. The composition according to claims 1 to 4 whereix said onum sate has the formula if
- COMPA CARON, and wherein A is an indomism, sufficiem, or dis-
- X is an organic sultonate countation, or a hatogenated metal or metalloid countanion 6. The composition according to claims 1 to 5 wherein said affin
- of polyteocyanises and compounds bearing at least two socyanise-reactive hydrogon atoms where the ratio 7. The composition according to claims 1 to 5 wherein said polyanethere precurates compres a meature of accyanate groups to accyanate-reactive hydrogen atoms is in the range 1.2 to 2.1. selected from the group consisting of acryteses, acrytesises and veryl compounds.
  - 8. A process comprising the steps of:
  - a) providing a polymenzable composition according to claims 1 to 7, and
- 9. A layered structure comprising a substrate having costed on one surface thereof the polymenizable c) allowing said months to polymence or acting energy to said months to effect polymentalities. composition according to claims 1 to 7.
  - 10. The layered structure according to claim 9 which is an imageable structure.
- 11. The preymentable composition according to claims 1 to 7 and 9 which has been curtiful.
  - 12. A shaped article according to claim 11.